

## PATTERNING METHOD WITH MICRO-CONTACT PRINTING AND ITS PRINTED PRODUCT

### BACKGROUND OF THE INVENTION

#### (1) Field of the Invention

The present invention relates to patterning method with micro-contact printing which makes possible to form micro-contact printed patterns with size as large as molecule used in the production of a variety of functional molecular device and DNA chip and printed product obtained by this method.

#### (2) Description of the Prior Art

In the field of molecular chemistry, L. Carter proposed the concept of molecular device in 1982. Research and development in this field has been actively carried out in enterprise, university and research institutes since that time. For example, if the specific function is given to each of organic molecules, respectively and assembly of these organic molecules is formed, the assembly of organic molecules makes possible the formation of semiconductor device with super-high integrated density such that there is no comparison between the integrated density of semiconductor device formed of the assembly of organic molecules and that of conventional semiconductor device. Further, in recent years, the genome analysis of DNA has been actively studied and the so-called biochip has attracted the attention of people. The application thereof is also thought for the development of biochip.

On the other hand, in photolithography employed until now as a method of reproducing micro-contact printed patterns, there is the limit for the reproduction of micro-contact printed patterns, in respect of mass-production of micro-contact printed patterns being made in a short time, since the substrate with desired micro-contact printed patterns

should be reproduced through several steps. Further, the photolithography is not suited for materials with low heat resistance and low mechanical resistance such as cells, DNA and enzymes, since the photolithography is carried out through complicated steps such as exposure, development and etching. Further, printing method makes possible the production of massive printed products. However, the reproduction of micro-contact printed patterns of the order of hundreds  $\mu$  m is the limit until now. Accordingly, printing method is not suited for the reproduction of micro-contact printed patterns.

Inventers of the present invention previously invented a method of reproducing micro-contact printed patterns comprising the steps of: forming patterns of molecules with the polarity on a substrate using molecular ink including molecules with the fixed polarity dispersed in solvent to form a first transfer layer and; forming patterns of molecules with the same polarity as the above-mentioned polarity or the different polarity from the above-mentioned polarity on the substrate using molecular ink including molecules with the same polarity as the above-mentioned polarity or the different polarity from the above-mentioned polarity (Japanese patent application No. 2000-151157).

However, in the above-mentioned method, density of ink used is lowered for increasing resolving power. The film of first transfer layer has defects since the first transfer layer is transferred using ink with thin density. When the second transfer layer is formed, ink for the second transfer layer comes in and contaminates the first transfer layer formed previously because area of the first transfer layer is not covered completely with ink for the first transfer layer, so that the contrast between the first transfer layer and the second transfer layer is lowered.

Further, there is a problem that if the density of ink for the first transfer layer is increased in order to remove defects of the first transfer

layer in forming the first transfer layer, the run and spread of ink occurs so that the resolving power is lowered.

#### BRIEF SUMMARY OF THE INVENTION

It is an object of the present invention to provide patterning method with micro-contact printing which makes possible to form briefly micro-contact printed patterns of molecular level with the contrast between a printed area and an unprinted area around the printed area, and its printed product.

Invention mentioned in claim 1, which solves the problem concerning patterning method with micro-contact printing, is characterized by patterning method with micro-contact printing comprising the steps of: applying resin on a master having projected patterns, hardening the resin and thereafter removing the hardened resin from the master to make a stamp of the resin; applying molecular ink including hydrophobic molecules dispersed in solvent on the stamp and forming micro-contact printed patterns of hydrophobic molecular layer on a substrate by means of the stamp on which the molecular ink is applied and; dipping the substrate with micro-contact printed patterns in hydrophilic molecule solution dispersed in solvent to give chemical modification to the areas of the surface of substrate around the micro-contact printed patterns, wherein solution including hydrophilic molecules having chain length shorter than the chain length of hydrophobic molecules included in the molecular ink is used as the hydrophilic molecule solution.

According to the present invention, micro-contact printed patterns formed of hydrophobic molecular layer formed on a substrate using hydrophobic molecular ink including hydrophobic molecules dispersed in solvent; the so-called micro-contact printed patterns are formed of hydrophobic molecules having chain length longer than the

chain length of hydrophilic molecules. Accordingly, in case that hydrophobic molecular layer has defects, when dipping an area of substrate uncovered with the hydrophobic molecular layer, namely unprinted area into hydrophilic solution, the hydrophilic solution comes in the defects. However, even in this case, since the hydrophilic molecules coming in the defects are covered with the hydrophobic molecules having chain length longer than that of the hydrophilic molecules, the high contrast between micro-contact printed patterns and unprinted area of hydrophilic molecules can be obtained without the hydrophobic property of micro-contact printed patterns being damaged.

Invention mentioned in claim 17, which solves the problem concerning printed product, is characterized by printed product provided with micro-contact printed patterns of hydrophobic molecules layer formed on a substrate using molecular ink including hydrophobic molecules dispersed in solvent and with hydrophilic molecule layer formed on areas of the surface of substrate around the micro-contact printed patterns, wherein the chain length of hydrophilic molecule is shorter than the chain length of hydrophobic molecules.

Invention mentioned in claim 20, which solves the problem concerning patterning method with micro-contact printing, is characterized by patterning method with micro-contact printing comprising the steps of: applying resin on a master having projected patterns, hardening the resin and thereafter removing the hardened resin from the master to make a stamp of the resin; applying molecular ink including hydrophilic molecules dispersed in solvent on the stamp and forming micro-contact printed patterns of hydrophilic molecular layer on a substrate by means of the stamp on which the molecular ink is applied and; dipping the substrate with micro-contact printed patterns in hydrophobic molecule solution including hydrophobic molecules

dispersed in solvent to give chemical modification to areas of the surface of substrate around the micro-contact printed patterns, wherein solution including hydrophobic molecules having chain length than the chain length of hydrophilic molecules included in the molecular ink is used as the hydrophobic molecule solution.

According to the patterning method with micro-contact printing as mentioned in claim 20, hydrophobic molecular layer is formed on an area of substrate around micro-contact printed patterns of hydrophilic molecular layer formed on a substrate using hydrophilic molecular ink including hydrophilic molecules dispersed in solvent. Accordingly, in case that hydrophobic molecular layer has defects, when dipping an area of substrate uncovered with the hydrophilic molecular layer, namely unprinted area into hydrophobic solution, the hydrophobic solution comes in the defects. However, even in this case, since the hydrophobic molecules coming in the defects are covered with the hydrophilic molecules having chain length longer than that of the hydrophobic molecules, the high contrast between micro-contact printed patterns and unprinted area of hydrophobic molecules can be obtained without the hydrophilic property of micro-contact printed patterns being damaged.

Invention mentioned in claim 36, which solves the problem concerning printed product, is characterized by printed product with micro-contact printed patterns of hydrophilic molecule layer formed on a substrate using molecular ink including hydrophilic molecules dispersed in solvent and with hydrophobic molecules layer formed on areas of the surface of substrate around the micro-contact printed patterns, wherein the chain length of hydrophobic molecules is shorter than the chain length of hydrophilic molecules.

Invention mentioned in claim 39 is characterized by patterning

method with micro-contact printing comprising the steps of: applying resin on a master having projected patterns, hardening the resin and thereafter removing the hardened resin from the master to make a stamp of the resin; applying molecular ink including hydrophobic molecules dispersed in solvent on the stamp and forming micro-patterns of hydrophobic molecular layer on a substrate by means of the stamp on which the molecular ink is applied and; dipping the substrate with micro-contact printed patterns in hydrophilic molecule solution including hydrophilic molecules dispersed in solvent to give chemical modification to areas of the surface of substrate around the micro-contact printed patterns, wherein after forming the micro-contact printed patterns, chemical modification is given to the areas of the surface of substrate around the micro-contact printed patterns by the hydrophilic molecular ink in the water.

According to the patterning method with micro-contact printing invention mentioned in claim 39, after forming the micro-contact printed patterns of hydrophobic molecular layer on a substrate using molecular ink including hydrophobic molecules dispersed in solvent, chemical modification is given to the areas of the surface of substrate around the micro-contact printed patterns by the hydrophilic molecular ink in the water under such a state that hydrophobic molecules are bonded with each other with hydrophobic bond in the water, so that the probability that hydrophilic molecules come in the hydrophobic molecular layer is low. Accordingly, the high contrast between micro-contact printed patterns and an area of substrate around the micro-contact printed patterns to which the chemical modification is given with the hydrophilic molecular ink can be obtained without the hydrophobic property of micro-contact printed patterns being damaged.

Invention mentioned in claim 41, which solves the problem

concerning patterning method with micro-contact printing, is characterized by patterning method with micro-contact printing comprising the steps of: applying resin on a master having projected patterns, hardening the resin and thereafter removing the hardened resin from the master to make a stamp of the resin; applying molecular ink including hydrophilic molecules dispersed in solvent on the stamp and forming micro-contact printed patterns formed of hydrophilic molecular layer on a substrate by means of the stamp on which the hydrophilic molecular ink is applied and; dipping the substrate with micro-contact printed patterns in hydrophilic molecule solution including hydrophilic molecules dispersed in solvent to give chemical modification to areas of the surface of substrate around the micro-contact printed patterns, wherein after forming the micro-contact printed patterns, chemical modification is given to the areas of the surface of substrate around the micro-contact printed patterns by the hydrophobic molecular ink in organic solution.

According to the patterning method with micro-contact printing invention mentioned in claim 41, after forming the micro-contact printed patterns of hydrophilic molecular layer on a substrate using molecular ink including hydrophilic molecules dispersed in solvent, hydrophobic molecular ink is applied on the areas of the surface of substrate around the micro-contact printed patterns in organic solution, so that the probability that hydrophilic molecules come in the hydrophobic molecular layer is low. Accordingly, the high contrast between micro-contact printed patterns and an area of substrate around the micro-contact printed patterns can be obtained without the hydrophobic property of micro-contact printed patterns being damaged.

Invention mentioned in claim 60, which solves the problem concerning printed product, is characterized by printed product provided

with micro-contact printed patterns of hydrophobic molecular layer formed on a substrate using hydrophobic molecular ink including hydrophobic molecules and hydrophilic molecular layer formed on areas of the surface of substrate around the micro-contact printed patterns, wherein the printed product is produced utilizing properties of hydrophobic molecules of the micro-contact printed patterns being cohesive by cohesive connection in the water.

Invention mentioned in claim 61, which solves the problem concerning printed product, is characterized by printed product provided with micro-contact printed patterns of hydrophilic molecular layer formed on a substrate using hydrophilic molecular ink including hydrophilic molecules and hydrophilic molecular layer formed on areas of the surface of substrate around the micro-contact printed patterns, wherein the printed product is produced utilizing properties of hydrophilic molecules of the micro-contact printed patterns being cohesive by hydrogen connection in the organic solution.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Figs. 1(a) through (f) is a schedule drawing showing the steps for forming micro-contact printed patterns having a first transfer layer and a second transfer layer on a substrate.

Figs. 2(a) and (b) are explanatory drawings of a method of applying molecular ink on a stamp.

Figs. 3(a) through (d) are views for explaining the effect shown by a difference between the chain length of hydrophobic molecules and that of hydrophilic molecules.

Figs. 4(a) through (s) are histograms showing results of adhering force between AFM chip and sample having micro-contact printed patterns measured in the water through chemical force microscope.

Fig. 5 shows an image obtained by the observation of micro-



contact printed patterns formed in a first example through chemical force microscope.

Figs. 6(a) through (e) is a schedule drawing showing a first part of the steps of forming micro-contact printed patterns of hydrophobic molecules on a substrate and giving chemical modification to the area of substrate around the micro-contact printed patterns by hydrophilic molecules according to invention mentioned in claim 39.

Fig. 7(a) through (b) is a schedule drawing showing a second part of the steps of forming micro-contact printed patterns on a substrate and giving chemical modification to the area of substrate around the micro-contact printed patterns following the steps shown in Figs 6 (a) through (e).

Figs. 8(a) and (b) are explanatory drawings of a method of applying molecular ink to a stamp.

Figs. 9(a) and (b) are views for explaining a method of forming micro-contact printed patterns of the present invention utilizing the hydrophobic bond.

Figs. 10 (a) through (e) is a schedule drawing showing a first part of the steps of forming micro-contact printed patterns of hydrophobic molecules on a substrate and giving chemical modification to the area of substrate around the micro-contact printed patterns by hydrophilic molecules according to invention mentioned in claim 41.

Figs. 11 (a) through (b) is a schedule drawing showing a second part of the steps of forming micro-contact printed patterns of hydrophobic molecules on a substrate and giving chemical modification to the area of substrate around the micro-contact printed patterns by hydrophilic molecules following the steps shown in Figs. 10 (a) and (b).

#### DETAILED DESCRIPTION

Then, a mode of the present invention is explained referring to

drawings.

Referring to Figs. 1(a) through (f), the steps of a first patterning method with micro-contact printing according to the present invention mentioned in claim 1 is explained.

First, as shown in Fig. 1(a), a master having projected patterns 1 with a desired height is formed. As materials of master 1 used is silicon or quartz or a laminate of a layer of silicon or quartz with a layer of metal or metal oxide. The projected pattern is of resist pattern 1a formed on the materials by photolithography or the ionizing radiation lithography such as electron beam lithography or AFM lithography. The height of projected patterns 1 is desirably about 1 through  $5\ \mu\text{m}$ .

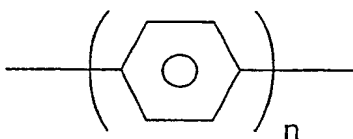
Then, as shown in Fig. 1(b), resin 2 is applied on the surface of master 1 with projected pattern, hardened and thereafter as shown in Fig. 1(c), the resin 2 is removed from the stamp 1, so that a stamp 3 of resin is formed. Resin of stamp 3 is preferably polydimethylsiloxane (PDMS). The polydimethylsiloxane is cast and hardened to form stamp 3.

Then, as shown in Fig. 1 (d), molecular ink 4 having hydrophobic molecules dispersed in solvent is applied on the stamp 3. Micro-contact printed patterns 6 of hydrophobic molecules are formed on a substrate 5 having the coating layer of gold, silver or copper on the surface of material such as glass plate by means of stamp 3.

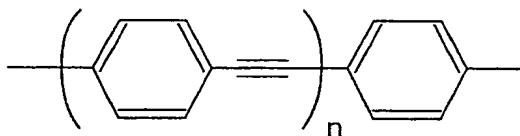
As molecular ink 4 having hydrophobic molecules dispersed in solvent used can be ink including any of molecules having SH group at the terminal thereof, silane coupler, or carboxylic acid, sulfonic acid, phosphonic acid, phosphoric acid or acid chloride thereof dispersed in organic solvent such as ethanol, toluene or methylene chloride or ethanol solution of alkanethiol  $\text{CH}_3(\text{CH}_2)_x\text{SH}$  or ink including molecules having the molecular formula represented by (X having part expressed

by any of the under-mentioned structural formula (1) through (7))—  
 $(\text{CH}_2)_n$ —(part expressed by any of the under-mentioned structural  
 formula (1) through (7)) —  $(\text{CH}_2)_m$ —Y in which m and  $n \geq 0$  and X  
 positioned at one end of the molecular formula is hydrophobic group and  
 Y positioned at the other end of the molecular formula is a group such as  
 $-\text{SH}$ ,  $-\text{COOH}$ ,  $-\text{SO}_3\text{H}$ ,  $-\text{PO}_3\text{H}$ ,  $\text{PO}_3\text{H}_2$ ,  $-\text{COCl}$ ,  $-\text{SO}_2\text{Cl}$ ,  $-\text{PO}_2\text{Cl}$   
 or  $-\text{PO}_2\text{Cl}_2$  dispersed in organic solvent such as ethanol,  
 toluene and methylene chloride.

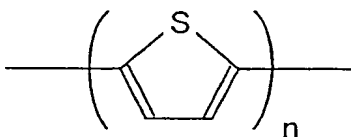
Structural formula (1)



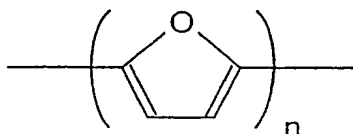
Structural formula (2)



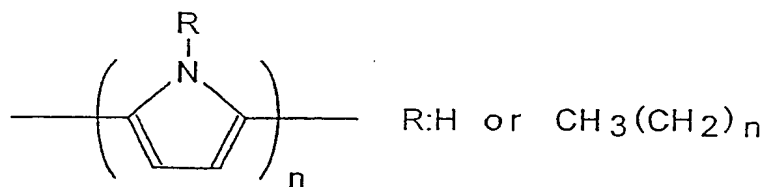
Structural formula (3)



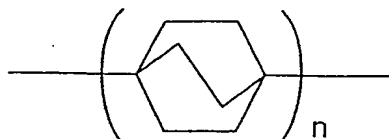
Structural formula (4)



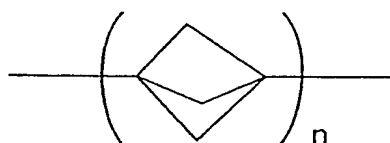
Structural formula (5)



Structural formula (6)



Structural formula (7)



In this case, when a substrate having coating layer of gold on the surface thereof is used as substrate, resolving power can be improved by the effect of self-organization of molecules included in the molecular ink.

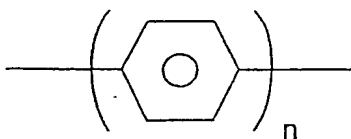
As a method of applying molecular ink 4 on the stamp 3 is given two methods shown in Fig. 2. A method shown in Fig. 2(a) is a wet inking method in which the whole surface of stamp 3 is applied by filling the whole surface of stamp 3 with molecular ink 4. A method shown in Fig. 2(b) is a contact inking method in which molecular ink 4 is applied only on the top surface of projected pattern by pushing the flat surface of PDMS resin 8 impregnated with molecular ink 4 against the stamp 3. The contact inking method is excellent in resolving power than in the wet inking method since the diffusion of molecular ink can be reduced in the contact inking method as compared with the wet inking method.

After forming micro-contact printed patterns 6 on substrate 5, the

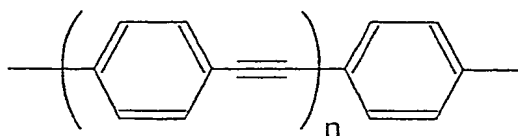
surface of substrate is dipped in hydrophilic molecular solution including hydrophilic molecules dispersed in solvent which have the chain length shorter than that of hydrophobic molecules included in molecular ink 4, by which chemical modification is given to an area of the surface of substrate uncovered with micro-contact printed patterns 6, as shown in Fig. 1(f), so that hydrophilic area 7 of hydrophilic molecules dispersed in solvent which have chain length shorter than that of hydrophobic molecules is formed on an area of the substrate uncovered with micro-contact printed pattern.

In the present invention, as hydrophilic molecular ink used is solution including molecules having the molecular formula represented by (X having part expressed by any of the under-mentioned structural formulas (1) through (7)) — (CH<sub>2</sub>)<sub>n</sub> — (part expressed by any of the under-mentioned structural formulas (1) through (7)) — (CH<sub>2</sub>)<sub>m</sub> — Y in which m and n  $\geq 0$  and X positioned at one end of the molecular formula is hydrophilic group and Y positioned at the other end of the molecular formula is a group being able to be connected with substrate such as —SH, —COOH, —SO<sub>3</sub>H, —PO<sub>3</sub>H, —PO<sub>3</sub>H<sub>2</sub>, —COCl, —SO<sub>3</sub>Cl, PO<sub>2</sub>Cl or —PO<sub>2</sub>Cl<sub>2</sub> dispersed in organic solvent such as ethanol, toluene or methylene chloride.

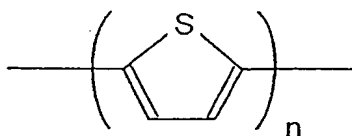
Structural formula (1)



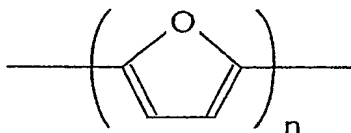
Structural formula (2)



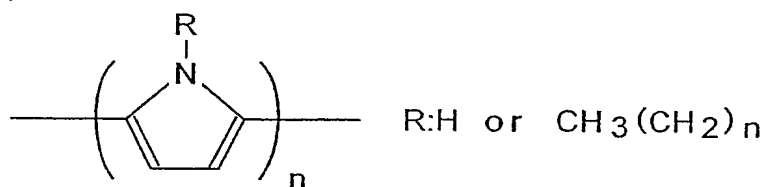
Structural formula (3)



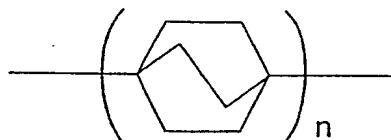
Structural formula (4)



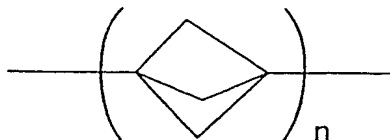
Structural formula (5)



Structural formula (6)



Structural formula (7)



Further, in the method of the present invention, as the hydrophilic molecular solution used can be hydrophilic molecules selected from among molecules having phosphoric acid group as hydrophilic group, molecules having sulfonic acid group as hydrophilic group, molecules

having amino group as hydrophilic group, molecules having hydroxyl group as hydrophilic group or molecules having carboxylic acid group as hydrophilic group dispersed in organic solvent such as ethanol, toluene or methylene chloride.

Or, in the present invention, as hydrophilic molecular solution used can be ethanol solution of  $\text{COOH}(\text{CH}_2)_y\text{—SH}$  having the chain length shorter than the chain length of alkanethiol  $\text{CH}_3(\text{CH}_2)_x\text{—SH}$ .

Accordingly, a hydrophilic area is formed around an area of micro-contact printed patterns, so that micro-contact printed patterns are formed with the high contrast between the micro-contact printed patterns and an area of substrate around micro-contact printed patterns.

In the present invention, if molecules included in hydrophobic molecular ink including hydrophobic molecules dispersed in solvent are molecules with molecules having SH group at terminal end dispersed in solvent, a substrate with the top coating layer of gold, silver or copper is desirably used as substrate on which micro-contact printed patterns are formed. In this case, resolving power is improved by the effect of self-organization.

In the present invention, if hydrophobic molecular ink including hydrophobic molecules dispersed in solvent includes silane coupler or carboxylic acid, sulfonic acid, phosphonic acid, phosphoric acid or acid chloride, substrate having the top coating layer of silicon oxide or metal oxide is desirably used as substrate on which micro-contact printed patterns are formed. In this case, resolving power is improved in the same way by the effect of self-organization.

In the present invention, if hydrophilic molecular ink including hydrophilic molecules dispersed in solvent includes silane coupler or carboxylic acid, sulfonic acid, phosphonic acid, phosphoric acid or acid chloride, substrate having the top coating layer of silicon oxide or metal

oxide is desirably used as substrate on which micro-contact printed patterns are formed. In this case, resolving power is improved in the same way by the effect of self-organization.

In the present invention, micro-contact printed patterns 6 can be formed of two or more of transfer layers formed using variety of ink containing different molecules.

In the present invention, as the molecular ink or the hydrophilic molecule solution used can be molecular ink or the hydrophilic molecule solution formed of polymer.

In the present invention, micro-contact printed patterns can be formed in order of micro-contact printed patterns of hydrophobic molecules with longer chain length.

Figs. 3(a) through (d) are explanatory drawings showing the effect shown by a difference between the chain length of hydrophobic molecules and that of hydrophilic molecules. As shown in Fig. 3(a), micro-contact printed patterns with gaps 11 are formed on the surface of substrate using  $\text{CH}_3(\text{CH}_2)_{11}\text{SH}$  such that the surface of substrate with the top coating layer of gold is insufficiently covered with  $\text{CH}_3(\text{CH}_2)_{11}\text{SH}$  molecules layer. Thereafter, the surface of substrate is dipped in solution of  $\text{COOH}(\text{CH}_2)_{15}\text{SH}$  having alkyl group with the chain length longer than that of  $\text{CH}_3(\text{CH}_2)_{11}\text{SH}$ , so that chemical modification is given to the area of the surface of substrate with the top coating layer of gold around the micro-contact printed patterns, wherein molecules of  $\text{COOH}(\text{CH}_2)_{15}\text{SH}$  come in the gaps 11 of micro-contact printed patterns as shown in Fig. 3(b). In this case, since molecule of  $\text{COOH}(\text{CH}_2)_{15}\text{SH}$  is longer than molecule of  $\text{CH}_3(\text{CH}_2)_{11}\text{SH}$ , COOH group of molecules of  $\text{COOH}(\text{CH}_2)_{15}\text{SH}$  is projected from between molecules of  $\text{CH}_3(\text{CH}_2)_{11}\text{SH}$ . Accordingly, the hydrophilic chemical modification given on an area of the surface of substrate around micro-contact printed patterns by



COOH(CH<sub>2</sub>)<sub>15</sub>SH results the reduction of the contrast between micro-contact printed patterns and area of the surface of substrate around the micro-contact printed patterns. On the other hand, when chemical modification is given to the area of the surface of substrate around the micro-contact printed patterns dipping the surface of substrate in solution of COOH(CH<sub>2</sub>)<sub>3</sub>SH having chain length shorter than that of CH<sub>3</sub>(CH<sub>2</sub>)<sub>11</sub>SH as shown in Fig. 3(c), molecules of COOH(CH<sub>2</sub>)<sub>3</sub>SH is covered with molecules of CH<sub>3</sub>(CH<sub>2</sub>)<sub>11</sub>SH as shown in Fig. 3(d). Accordingly, the contrast between micro-contact printed patterns and area of the surface of substrate around the micro-contact printed patterns is not reduced.

Figs. 4(a) through (c) are histograms showing results of adhering force between AFM (atomic force microscope) chip with the top coating layer of gold to which chemical modification is given by 1 ml of 1-eicosanethiol and the sample having micro-contact printed patterns measured in the water through chemical force microscope, wherein each coordinate has orthogonal coordinate system with interaction (nN) as abscissa and frequency as coordinate.

Fig. 4(a) shows histogram of interaction in case that micro-contact printed patterns are formed with CH<sub>3</sub>(CH<sub>2</sub>)<sub>11</sub>SH and chemical modification is given to the area of the surface of substrate around the micro-contact printed patterns with COOH(CH<sub>2</sub>)<sub>15</sub>SH, wherein two peaks approach each other. Accordingly, it is understood that the contrast between the area of micro-contact printed patterns and the area of the surface of substrate around the micro-contact printed patterns is low.

Fig. 4(b) shows histogram of interaction in case that micro-contact printed patterns are formed with CH<sub>3</sub>(CH<sub>2</sub>)<sub>11</sub>SH and chemical modification is given to the area of the surface of substrate micro-

contact printed patterns with  $\text{COOH}(\text{CH}_2)_{10}\text{SH}$ , wherein the interval between two peaks become wider as compared with a case shown in Fig. 4(a). Accordingly, it is understood that the contrast between the area of micro-contact printed patterns and the area of the surface of substrate around the micro-contact printed patterns is somewhat found.

Fig. 4(c) shows histogram of interaction in case that micro-contact printed patterns are formed with  $\text{CH}_3(\text{CH}_2)_{11}\text{SH}$  and chemical modification is given to the area of the surface of substrate around the micro-contact printed patterns with  $\text{COOH}(\text{CH}_2)_3\text{SH}$ , wherein two peaks are distant largely from each other. Accordingly, it is understood that the contrast between the area of micro-contact printed patterns and the area of the surface of substrate around the micro-contact printed patterns is apparently found.

As mentioned hereinbefore, in patterning method with micro-contact printing comprising the steps of: applying resin on a master having projected patterns, hardening the resin and thereafter removing the hardened resin from the master to make a stamp of the resin; applying molecular ink including hydrophobic molecules dispersed in solvent on the stamp and forming micro-contact printed patterns of hydrophobic molecular layer on a substrate by means of the stamp on which the molecular ink is applied and; dipping the substrate with micro-contact printed patterns in hydrophilic molecule solution dispersed in solvent to give chemical modification to the areas of the surface of substrate around the micro-contact printed patterns, solution including hydrophilic molecules having chain length shorter than the chain length of hydrophobic molecules included in the molecular ink is used as the hydrophilic molecule solution. However, micro-contact printed patterns may be produced also by patterning method with micro-contact printing comprising the steps of: applying resin on a

master having projected patterns, hardening the resin and thereafter removing the hardened resin from the master to make a stamp of the resin; applying molecular ink including hydrophilic molecules dispersed in solvent on the stamp and forming micro-contact printed patterns of hydrophilic molecular layer on a substrate by means of the stamp on which the molecular ink is applied and; dipping the substrate with micro-contact printed patterns in hydrophobic molecule solution including hydrophobic molecules dispersed in solvent to give chemical modification to areas of the surface of substrate around the micro-contact printed patterns, wherein solution including hydrophobic molecules having chain length than the chain length of hydrophilic molecules included in the molecular ink is used as the hydrophobic molecule solution.

In this case, ink mentioned in any of claims 23 through 25 can be used as molecular ink including hydrophilic molecules dispersed in solvent.

Solution mentioned in any of claims 26 through 28 can be used as hydrophobic solution.

Then, referring to Figs. 6(a) through (e), the process of patterning method with micro-contact printing of the present invention mentioned in claim 39 is explained.

First, as shown in Fig. 6(a), a master 1 having the produced pattern with a desired height is produced. As materials of the master 1 used is a layer of silicon or quartz or a laminate of a layer of silicon or quartz with a layer of metal or metal oxide. Then, projected patterns are formed with resist, silicon or quartz metal or oxide thereof or nitride thereof 1a by photolithography or the ionizing radiation lithography such as electron beam lithography or AFM lithography. The height of the projected patterns is desirably about 1 trough  $5\ \mu\text{m}$ .

Then, as shown in Fig. 6(b), resin 2 is applied on the surface of master 1 having projected patterns and then the resin 2 is removed from the master 1 by which stamp 3 made of resin is formed as shown in Fig. 6(c). Polydimethylsiloxane (PDMS) is preferably used as resin forming stamp 3. The stamp 3 is formed after the master by a method comprising the steps of spin-coating the PDMS resin on the surface of master, hardening the PDMS resin and then removing the hardened resin from the master.

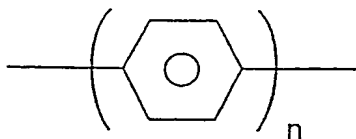
Then, as shown in Fig. 6(d), molecular ink 14 including hydrophobic molecules dispersed in solvent is applied on the stamp 3 and micro-contact printed patterns 16 made of hydrophobic molecules are formed on the surface of substrate 5 with the top coating layer of gold using the stamp 3.

Ink including any of molecule having SH group at the terminal thereof, silane coupler, or carboxylic acid, sulfonic acid, phosphonic acid, phosphoric acid or acid chloride thereof can be used as the molecular ink 14 including hydrophobic molecules dispersed in solvent. In this case, when using the substrate with the top coating layer of gold as substrate, resolving power is improved by the effect of self-organization of molecules included in the molecular ink.

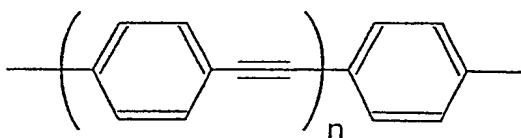
Further, as hydrophobic molecular ink used can be ink including molecules having the molecular formula represented by ( $X_1$  having part expressed by any of the under-mentioned structural formulas (1) through (7)) —  $(CH_2)_n$  — (part expressed by any of the under-mentioned structural formulas (1) through (7)) —  $(CH_2)_m$  — Y in which  $m$  and  $n \geq 0$  and  $X_1$  positioned at one end of the molecular formula is hydrophobic group and Y positioned at the other end of the molecular formula is a group being able to be connected with substrate such as —SH, —COOH, —SO<sub>3</sub>H, —PO<sub>3</sub>H, —PO<sub>3</sub>H<sub>2</sub>, —COCl, —SO<sub>3</sub>Cl, PO<sub>2</sub>Cl

or  $-\text{PO}_2\text{Cl}_2$  dispersed in organic solvent such as ethanol, toluene or methylene chloride.

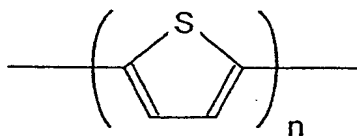
Structural formula (1)



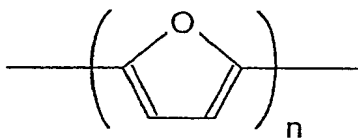
Structural formula (2)



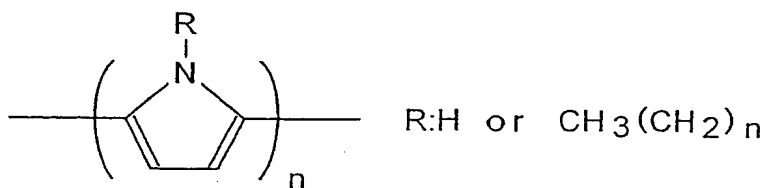
Structural formula (3)



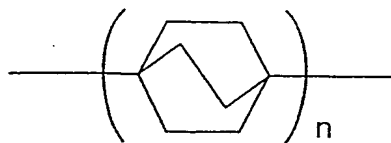
Structural formula (4)



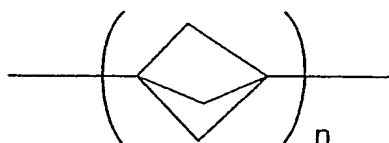
Structural formula (5)



Structural formula (6)



Structural formula (7)



There are two methods as applying methods of molecular ink 14 on the stamp 3 as shown in Figs. 8(a) and (b). A method shown in Fig. 8(a) is a wet inking method in which the whole surface of stamp 3 is applied by filling the whole surface of stamp 3 with molecular ink 4. A method shown in Fig. 2(b) is a contact inking method in which molecular ink 4 is applied only on the top surface of projected pattern by pushing the flat surface of PDMS resin 8 impregnated with molecular ink 4 against the stamp 3. The contact inking method is excellent in resolving power than in the wet inking method since the diffusion of molecular ink can be reduced in the contact inking method as compared with the wet inking method.

Then, as shown in Fig. 7(a), the substrate 5 with micro-contact printed patterns 16 is dipped in water 9. Hydrophobic molecules forming micro-contact printed patterns 16 are hydrophobic-bonded with each other to form the assembly of hydrophobic molecules. Accordingly, faultless micro-contact printed patterns are formed.

Then, chemical modification is given to an area of the surface of substrate 5 uncovered with the micro-contact patterns 16 made of molecules hydrophobic-bonded using solution of  $\text{COOH}(\text{CH}_2)_Y-\text{SH}$

dispersed in water or solution of  $\text{COOH}(\text{CH}_2)_Y-\text{SH}$  dispersed in KOH aqueous solution. Accordingly, hydrophilic area 17 is formed around the micro-contact printed patterns without damaging the hydrophobic property of the area of hydrophobic micro-contact printed patterns, so that the micro-contact printed patterns can be formed with the high contrast between the micro-contact printed patterns and the areas of substrate around the micro-contact printed patterns.

Further, in patterning method with micro-contact printing of the present invention, a chemical modification is given to the surface of substrate around micro-contact printed patterns by hydrophilic molecular ink in the water, and thereafter further chemical modification can be given with a high degree to the area of surface of substrate around the micro-contact printed patterns with hydrophobic molecules.

Fig. 9 is a view explaining the effect of patterning method with micro-contact printing of the present invention utilizing hydrophobic-bond. Fig. 9(a) shows schematically hydrophobic molecular layer 160 formed dipping the formed micro-contact printed patterns 16 in the water in the state of assembly of hydrophobic molecules hydrophobic-bonded with each other. As apparent from this, an area of the micro-contact printed patterns 16 is covered with assembled hydrophobic molecular layer 160 so that micro-contact printed patterns having few defects are formed. Namely, the film of micro-contact printed patterns 16 is formed without exposing the surface of substrate under the micro-contact printed patterns.

Then, chemical modification is given to the area of surface of substrate around the micro-contact printed patterns 16 using solution of  $\text{COOH}(\text{CH}_2)_Y-\text{SH}$  dispersed in water or solution of  $\text{COOH}(\text{CH}_2)_Y-\text{SH}$  dispersed in KOH aqueous solution. Accordingly, hydrophilic area 17 is formed around the micro-contact printed patterns without damaging the

hydrophobic property of the area of hydrophobic micro-contact printed patterns as shown in Fig. 9(b), so that the micro-contact printed patterns 16 can be formed with the high contrast between the micro-contact printed patterns 16 of hydrophobic molecular layer 160 and the areas of substrate around the micro-contact printed patterns 16.

Further, in the above-mention invention, hydrophilic chemical modification is given to the area of surface of substrate around the micro-contact printed patterns and then further chemical modification can be given with high degree to an area of the micro-contact printed patterns using hydrophobic ink in alcoholic solution or hydrophobic molecules can be transferred on the micro-contact printed patterns using the stamp having hydrophobic ink applied thereon. Parts of defects of micro-contact printed patterns are mended perfectly in the second process.

Micro-contact printed patterns can be observed using AFM (atomic force microscope) chip with the top coating layer of gold to which chemical modification is given by 1 ml of 1-eicosanethiol by means of chemical force microscope.

Then, referring to Figs. 10(a) through (e), patterning method with micro-contact printing of the present invention mentioned in claim 41 is explained.

First, as shown in Fig. 10(a), a master 1 having projected patterns with a desired height is formed. As materials of the master 1 used is silicon or quartz or a laminate of a layer of silicon or quartz with a layer of metal or metal oxide. The projected pattern is formed of pattern of resist, silicon or quartz with a layer of metal or metal oxide or metallic nitride 1a. The height of projected patterns 1 is desirably about 1 through 5  $\mu$  m.

Then, as shown in Fig. 10(b), resin 2 is applied on the surface of



master 1 having projected patterns 1a, hardened and then the hardened resin 2 is removed from the master 1 so that the stamp 3 made of resin is formed as shown in Fig. 10(c). Polydimethylsiloxane (PDMS) is preferably used as resin forming stamp 3. The stamp is formed after the master by a method comprising the steps of spin-coating the PDMS resin on the surface of master, hardening the PDMS resin and then removing the hardened resin from the master.

Then, as shown in Fig. 10(d), molecular ink 24 including hydrophilic molecules dispersed in solvent is applied on the stamp 3 and micro-contact printed patterns 26 made of hydrophilic molecules are formed on the surface of substrate 5 with the top coating layer of gold.

Ink including molecules positioned opposite molecules connected to substrate and selected from among molecules having phosphoric acid, molecules having phosphonic acid group, or molecules having amino group, molecules having hydroxyl group dispersed in solvent can be used as hydrophilic molecular ink 24. In this case, when using substrate with the top coating layer of silicon oxide or metal oxide, resolving power is improved by the effect of self-organization.

As a method of applying molecular ink 24 on the stamp 3 is given two methods of a wet inking method and a contact inking method, as mentioned in the description on patterning method with micro-contact printing of the present invention mentioned in claim 39. The contact inking method is excellent in resolving power than in the wet inking method since the diffusion of molecular ink can be reduced in the contact inking method as compared with the wet inking method.

Then, as shown in Fig 11(a), a substrate 5 having micro-contact printed patterns 26 is dipped in organic solution 28. Since organic solution 28 is difficult to be mixed with hydrophilic molecules forming the micro-contact printed patterns 26 and hydrophilic molecules are

cohered by hydrogen bond with each other, the probability that hydrophobic molecules are adhered to micro-contact printed patterns in the process of chemical modification being given to the area of surface of substrate around the micro-contact printed patterns in solution including hydrophobic molecules is low. Accordingly, the area 27 to which chemical modification is given is formed around the micro-contact printed patterns without damaging the hydrophilic property of the area of hydrophilic micro-contact printed patterns, so that micro-contact printed patterns with the high contrast between the micro-contact printed patterns and the area of surface of substrate around the micro-contact printed patterns can be formed.

In the above-mentioned invention, after chemical modification is given by organic solution including hydrophobic molecular ink, the second chemical modification can be further given to micro-contact printed patterns in alcoholic solution of hydrophilic molecular ink or hydrophilic molecules can be transferred on the micro-contact printed patterns using a stamp on which hydrophilic molecular ink is applied. In the second process, parts of defects in micro-contact printed patterns can be perfectly mended.

Micro-contact printed patterns formed as above-mentioned can be observed using AFM (atomic force microscope) chip with the top coating layer of gold to which chemical modification is given by 1 ml of 1-eicosanethiol by means of chemical force microscope.

In the above-mentioned invention, in patterning method with micro-contact printing comprising the steps of: applying resin on a master 1 having projected patterns, hardening the resin and thereafter removing the hardened resin from the master 1 to make a stamp 3 of the resin; applying hydrophilic molecular ink including hydrophilic molecules dispersed in solvent on the stamp 3 and forming micro-contact printed

patterns 26 formed of hydrophilic molecular layer on a substrate by means of the stamp on which the hydrophilic molecular ink is applied and; dipping the substrate with micro-contact printed patterns in hydrophilic molecule solution including hydrophilic molecules dispersed in solvent to give chemical modification 27 to areas of the surface of substrate around the micro-contact printed patterns, wherein after forming the micro-contact printed patterns 26, second chemical modification 27 is given to the areas of the surface of substrate around the micro-contact printed patterns 26 by the hydrophilic molecular ink in the water.

According to the above-mentioned method of present invention, printed product can be obtained which are provided with micro-contact printed patterns formed of hydrophobic molecular layers formed on a substrate using molecular ink including hydrophobic molecules dispersed in solvent and hydrophilic molecular layers formed on the area of surface of the substrate around the micro-contact printed patterns, wherein the chain length of hydrophilic molecules is shorter than the chain length of hydrophobic molecules.

Further, instead of producing the printed product as mentioned hereinbefore, printed product can be also obtained by patterning method with micro-contact printing comprising the steps of: applying resin on a master having projected patterns, hardening the resin and thereafter removing the hardened resin from the master to make a stamp of the resin; applying molecular ink including hydrophilic molecules dispersed in solvent on the stamp and forming micro-contact printed patterns of hydrophilic molecular layer on a substrate by means of the stamp on which the hydrophilic molecular ink is applied and; dipping the substrate with micro-contact printed patterns in hydrophilic molecule solution including hydrophilic molecules dispersed in solvent to give chemical

modification to areas of the surface of substrate around the micro-contact printed patterns, wherein after forming the micro-contact printed patterns, chemical modification is given to the areas of the surface of substrate around the micro-contact printed patterns by the hydrophobic molecular ink in organic solution.

In this case, after giving chemical modification to the areas of the surface of substrate around the micro-contact printed patterns by hydrophobic molecular ink in organic solution, chemical modification can be further given to the micro-patterns at the higher density to the micro-contact printed patterns in alcoholic solution or hydrophilic molecules may be again transferred on the micro-contact printed patterns using a stamp filled with hydrophilic molecules. In the second process, parts of defects in micro-contact printed patterns can be perfectly mended.

Further, as hydrophobic molecular ink including hydrophobic molecules dispersed in solvent can be used hydrophobic molecular ink mentioned in any of claims 45, 46 and 50.

Further, as hydrophilic molecular ink including hydrophilic molecules dispersed in solvent can be used hydrophilic molecular ink including hydrophilic molecules dispersed in solvent mentioned in any of claims 47, 48 and 51.

Then, patterning method with micro-contact printed printing of the present invention is explained further in detail giving examples.

(Example 1)

First, a thin film of chromium was formed on a surface of quartz plate by the sputtering method. Resist patterns with the thickness of 4000 Å were formed on the quartz plate with the thin film of chromium to form a master with a height on the surface of the quartz plate with the thin film of chromium. PDMS resin was spin-coated or cast on the

surface of the master with resist patterns and was heat-treated at 65°C for four hours to be hardened. Thereafter, the hardened PDMS resin was removed from the master to form a stamp. Then, molecular ink including ethanol solution of  $\text{CH}_3(\text{CH}_2)_{19}\text{SH}$  was applied on the stamp by the contact inking method.

On the other hand, a substrate with evaporation layer of gold on a glass plate was provided. The stamp having the molecular ink on the surface thereof was pressed against the surface of substrate by which the molecular ink was transferred to the substrate. Thereby, micro-contact printed patterns were formed.

Then, chemical modification was given to the area of surface of substrate around the micro-contact printed patterns using ethanol solution of  $\text{COOH}(\text{CH}_2)_{10}\text{SH}$  so that printed product is formed.

Fig. 5 shows an image of the printed product observed through the chemical force microscope. In Fig. 5, A indicates the hydrophobic area and B indicates the hydrophilic area.

(Comparative Example)

The same process as in Example 1 was carried out for the formation of micro-contact printed patterns except molecular ink of ethanol solution of  $\text{CH}_3(\text{CH}_2)_{10}\text{SH}$  was used instead of molecular ink of ethanol solution of  $\text{CH}_3(\text{CH}_2)_{19}\text{SH}$  for the formation of micro-contact printed patterns and  $\text{COOH}(\text{CH}_2)_{20}\text{SH}$  was used instead of ethanol solution of  $\text{COOH}(\text{CH}_2)_{10}\text{SH}$  for the chemical modification given to the area of surface of substrate around the micro-contact patterns. However, resolution of micro-contact patterns was impossible since the contrast between the micro-contact printed patterns and the area of surface of substrate around the micro-contact printed patterns was low.

(Example 2)

First, a thin film of chromium was formed on a surface of quartz

plate by the sputtering method. Resist patterns with the thickness of 4000 Å were formed on the quartz plate with the thin film of chromium to form a master with a height on the surface of the quartz plate with the thin film of chromium. PDMS resin was spin-coated on the surface of the master with resist patterns and was heat-treated at 65°C for four hours to be hardened. Thereafter, the hardened PDMS resin was removed from the master to form a stamp. Then, molecular ink including ethanol solution of  $\text{CH}_3(\text{CH}_2)_{19}\text{SH}$  was applied on the stamp by the contact inking method.

On the other hand, a substrate with evaporation layer of gold on a glass plate was provided. The stamp having the molecular ink on the surface thereof was pressed against the surface of substrate so that the molecular ink was transferred to the substrate. Thereby, micro-contact printed patterns were formed.

Then, the substrate with the micro-contact printed patterns was dipped in the water so that  $\text{CH}_3(\text{CH}_2)_{19}\text{SH}$  was hydrophobic-bonded to be cohered. Then, chemical modification was given to the area of surface of substrate around the micro-contact printed patterns using aqueous solution of  $\text{COOH}(\text{CH}_2)_{10}\text{SH}$  under the above-mentioned state. Thereby, printed product with high contrast between the micro-contact printed patterns and the area of surface of substrate around the micro-contact printed patterns was formed.

(Example 3)

After forming of printed product according to Example, chemical modification by hydrophobic molecules was again given to the micro-contact printed patterns using a stamp filled with hydrophobic ink. In the second process, parts of defects in micro-contact printed patterns can be perfectly mended. Thereby, printed product with further higher contrast between the micro-contact printed patterns and the area of

surface of substrate around the micro-contact printed patterns was formed.

(Example 4)

According to Example 2, after chemical modification of the area of surface of substrate around the micro-contact printed patterns by hydrophilic molecules, further chemical modification was given to the micro-contact printed patterns at the higher density by hydrophobic molecules included in alcoholic solution of hydrophobic molecules. In this process, parts of defects of the micro-contact printed patterns was perfectly mended so that printed product having the further higher contrast between the micro-contact printed patterns and the area of surface of substrate around the micro-contact printed patterns could be obtained.

(Example 5)

The same process as in Example 4 was carried out except a substrate having a coating of silicon oxide thereon was a substrate and ethanol solution of  $\text{OH}(\text{CH}_2)_{10}\text{COOH}$  was used as molecular ink, in which micro-contact printed patterns of hydrophilic molecules was formed on the substrate.

Then, the substrate having the micro-contact printed patterns was dipped in benzene solution of  $\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$  and in this state, chemical modification by  $\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$  was given to the surface of substrate around the micro-contact printed patterns so that printed product having the high contrast between the micro-contact printed patterns and the area of surface of substrate around the micro-contact printed patterns was formed.

(Example 6)

After forming printed product according to Example 3, chemical modification of hydrophilic molecules was again given to the micro-

contact printed patterns using a stamp filled with hydrophilic ink. In this process, parts of defects of the micro-contact printed patterns were perfectly mended so that printed product having the further higher contrast between the micro-contact printed patterns and the area of surface of substrate around the micro-contact printed patterns could be obtained.

(Example 7)

After chemical modification by hydrophilic molecules being given to the area of surface of substrate around the micro-contact printed patterns in the water according to Example 5, further chemical modification was given to the micro-contact printed patterns at the higher density in alcoholic solution. In this process, parts of defects of the micro-contact printed patterns were perfectly mended so that printed product having the further higher contrast between the micro-contact printed patterns and the area of surface of substrate around the micro-contact printed patterns could be obtained.

As mentioned hereinbefore according to the invention mentioned in claim 1, in patterning method with micro-contact printing comprising the steps of: applying resin on a master having projected patterns, hardening the resin and thereafter removing the hardened resin from the master to make a stamp of the resin; applying molecular ink including hydrophobic molecules dispersed in solvent on the stamp and forming micro-contact printed patterns formed of hydrophobic molecular layer on a substrate by means of the stamp on which the molecular ink is applied and; dipping the substrate with micro-contact printed patterns in hydrophilic molecule solution dispersed in solvent to give chemical modification to the areas of the surface of substrate around the micro-contact printed patterns, solution including hydrophilic molecules having chain length shorter than the chain length of hydrophobic molecules



included in the molecular ink is used as the hydrophilic molecule solution. According to this, printed product having the contrast between the micro-contact printed patterns and the area of surface of substrate around the micro-contact printed patterns can be briefly formed.

Further, as mentioned in claim 20, in patterning method with micro-contact printing comprising the steps of: applying resin on a master having projected patterns, hardening the resin and thereafter removing the hardened resin from the master to make a stamp of the resin; applying molecular ink including hydrophilic molecules dispersed in solvent on the stamp and forming micro-contact printed patterns of hydrophilic molecular layer on a substrate by means of the stamp on which the molecular ink is applied and; dipping the substrate with micro-contact printed patterns in hydrophobic molecule solution including hydrophobic molecules dispersed in solvent to give chemical modification to areas of the surface of substrate around the micro-contact printed patterns, solution including hydrophobic molecules having chain length than the chain length of hydrophilic molecules included in the molecular ink is used as the hydrophobic molecule solution. According to this patterning method, printed product having micro-contact printed patterns with the high contrast between the micro-contact printed patterns and the area of surface of substrate around the micro-contact printed patterns can be also similarly formed. Further, since it is unnecessary to increase the density of ink to get rid of defects from the micro-contact printed patterns in forming the micro-contact printed patterns, the reduction of resolving power produced by run and spread of ink can be avoided.

Further, according to patterning method with micro-contact printing of the present invention mentioned in claim 39, since after forming the micro-contact printed patterns of hydrophobic molecular

layer formed on a substrate using molecular ink including hydrophobic molecules dispersed in solvent, chemical modification is given to the areas of the surface of substrate around the micro-contact printed patterns by the hydrophilic molecular ink in the water under the state that hydrophobic molecules are hydrophobic-bonded with each other, the probability of hydrophilic molecules coming in hydrophobic molecular layer is low. As a result, the contrast between the micro-contact printed patterns chemical-modified by hydrophilic molecules and the area of surface of substrate around the micro-contact printed patterns can be obtained without damaging the hydrophobic property of micro-contact patterns.

Further, according to patterning method with micro-contact printing mentioned in claim 41, after forming the micro-contact printed patterns of hydrophilic molecular layer formed on a substrate using molecular ink including hydrophilic molecules, chemical modification is given to the areas of the surface of substrate around the micro-contact printed patterns by the hydrophobic molecular ink in organic solution. Accordingly, the probability of hydrophobic molecules coming in the hydrophilic molecular layer is low. As a result, the contrast between the micro-contact printed patterns chemical-modified by hydrophilic molecules and the area of surface of substrate around the micro-contact printed patterns can be obtained without damaging the hydrophilic property of micro-contact patterns.

Printed product of the present invention can be utilized for the connection of specified molecules, immobilization of enzyme, cell or DNA and others, utilizing the combination of different properties of surfaces in printed products.